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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

Final Report

Chemical Processes During the Starved Air Incineration of Municipal Solid Waste

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Abstract

Thermal analytical measurements on the pyrolytic and oxidative decomposition of municipal solid waste and its constituent parts (cellulose, sawdust, newsprint and polyethylene) have been carried out. Under pyrolytic conditions thermogravimetric analysis of municipal solid waste indicated minimum yields of char in the 10% range. Evolved gas analysis yielded information regarding the nature of the volatile gases in terms of total FID sensitive hydrocarbons, CO, CO_2 and CH_4. From material balance considerations it is concluded that the volatile gases includes large quantities of acidic carbonyl and alcohol compounds. The total quantity of volatile gases not including the directly analyzed light gases, is of the order of 60%. The overall process is thermally neutral. This is in good agreement with measurements using larger samples. Under oxidative conditions MSW ignited very easily and the reaction goes rapidly to completion. Combination of the experimental data and literature information leads to a description of the chemical processes in starved air incineration.

Introduction

This paper contains the results of an investigation into the nature and heat content of the substances formed during the pyrolysis and partial oxidation of municipal solid waste. The information is to be used as inputs to a computer model for starved air incineration currently being developed by C. A. Kodres at the Naval Civil Engineering Laboratory (1). A schematic of a starved air incineration system can be found in Figure I. During operation, partial oxidation with under and/or overfired air occurs in the primary combustion chamber. Complete combustion is effected in the secondary combustion chamber and followed by heat recovery. Such devices offer advantages with respect to completeness of combustion. A key variable in modeling such systems is the nature and heat content of the gas that is carried over into the secondary combustion chamber. This is not a simple and straightforward problem as evidenced by the fact that even for as thoroughly studied a subject as coal the nature and rates of the devolatization process is still a subject of research,controversy and uncertainty (2). In the following, we begin with background material on the nature of municipal waste. This will be followed by a discussion of reaction mechanisms for the decomposition of the generic chemical components and how such considerations will be reflected in the heating values of the product gases. We then describe our thermal analytical studies. Finally, we discuss the implication of our results in terms of earlier work and conclude with a number of recommendations.

Background

Municipal solid waste is a heterogeneous mixture of organic and inorganic substances. Tables Ia-d contains representative data (1, 3-5). It is indicative of the difficulties inherent in attempting to describe its proper-

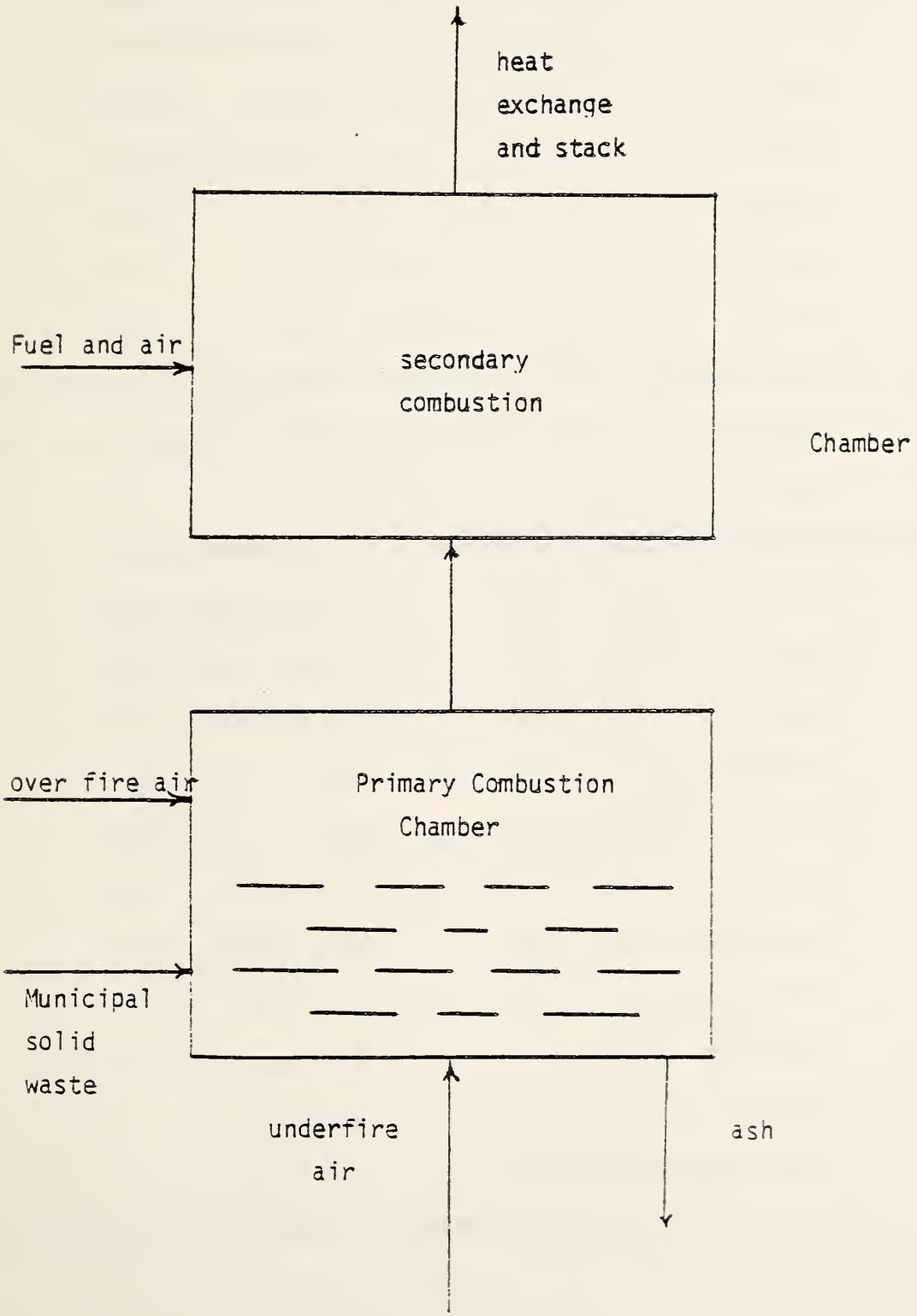


Figure I: Schematic of starved air incinerator

Table I: Representative Data Regarding
the Composition of Municipal Solid Waste

a) Quad-City Solid Wastes Project First Annual Report Fact Sheet (%) (3)

paper	39.8 - 53.66
wood	1.69 - 3.45
plastic	2.33 - 2.97
glass	3.73 - 9.96
metal	6.95 - 12.91
stone-sand	6.16 - 8.53
organics*	20.22 - 26.76
rags	2.2 - 7.6

b) Municipal Waste Generation in 1971 (4)

paper	31.8
wood	3.7
plastics	3.4
glass	9.7
metals	9.5
food wastes	17.6
yard wastes	19.3
rubber and leather	2.4
textiles	1.4
miscellaneous inorganic	1.4

c) Composition of Organic Waste at NAS, Jacksonville (1)

paper	34.7
corrugated bases	27.9
plastics	14.8
food waste	17.1
textile	1.2
grass	2.1
wood	2.2

d) Composition of MSW obtained January 10-21, 1984 from the Baltimore County Resource and Recovery Facility; 10 samples (5)

initial moisture	22 - 52.7
metal (magnetic)	.3 - 6.4
metal (non-magnetic)	.6 - 1.9
wood, vegetable	.2 - 2.5
textiles	.5 - 13.8
plastics	3.3 - 12.8
paper	57.9 - 67.7
glass, ceramic	.3 - 3.5
fines	9.7 - 23.6
metals	1.2 - 10.7

* Assume to be food, yard wastes and miscellaneous organics.

ties. In terms of chemical effects we note the presence of large quantities of cellulosic products; specifically, newsprint, wood, food and yard wastes. In the case of wood and yard wastes there are also considerable quantities of lignin. Together with plastics, rubber, textiles and leather they represent other types of organic polymers. They differ from cellulose in terms of a much lower oxygen content. This leads to higher heating values. From the generic chemical point of view the processes occurring in the primary combustion chamber are dominated by depolymerization and condensation reactions of cellulose and with varying contributions from other man-made and natural polymers. The inorganics are not of concern with respect to heating values. However, they have important effects with regard to catalyzing or transforming the nature of the decomposition process. This can be an important uncertainty. In addition, on a weight basis the most important inorganic compound is water. Since it has no heating value its principal role will be as a diluent. Unfortunately, the quantities present can vary greatly. In any model, water content must be an adjustable parameter.

The general question of the variability of municipal solid waste has been treated in detail at the National Bureau of Standards (5). Over a two week period, samples of municipal solid waste at the Baltimore County Resource Facility in Cockeysville, Maryland which have passed through the primary shredder were collected daily. The total moisture content was determined and after reduction to particle sizes of 2 mm or less 40 samples were prepared for measurement. Properties determined included residual moisture, furnace ash, bomb ash and higher heating value. The important conclusion reached was that while moisture and ash showed wide variations, close to 40%, the higher heating value (moisture and ash free) of the combustible fraction showed variations of only 4%. This is indicative of the kind of variation in

combustion related properties that can be expected at a particular locality and over a limited period of time. It is a necessary condition for serious work in this area. Much of our experimental results will be based on these samples.

There is considerable qualitative understanding of the mechanism of decomposition of the various components in municipal solid waste. The quantitative situation is, and probably will remain so for many years, unsatisfactory. This is due to the problems inherent in studying chemical processes involving organic solids. Specifically, during the decomposition process compounds are produced which are chemically and thermally less stable than the starting material. There is competition between escaping from the solid (volatilization) or undergoing further reactions (condensation, ultimately leading to char formation). As a result it is not possible to isolate individual processes for study and then creating via computer simulation directly observable events. Instead, all that is available are global observations which are influenced strongly by the physical parameters of the experiments. These include heating rates, sample size, sample state, etc. Nevertheless the existing data are suggestive and set a basis for further work.

Cellulose begins to decompose at temperature above 300°C. From differential scanning calorimetric (DSC) measurements, the reactions appear to be mildly endothermic. Interestingly,the degree of endothermicitly is controlled by the crystallinity of the sample (6). From our DSC tests with newsprint the heat of reaction is close to neutral. However note that we are describing a devolatilization process. The heat measured in DSC experiment represent that which is transferred to the sensing elements. The exact significance with respect to the total system is unclear. The initial depolymerization product

is levoglucosan (1,6 anhydro-β-D-glucopyranose) and a number of its isomers. This is accompanied and followed by dehydration processes leading to unsaturated compounds such as levoglucosenone, furfural etc. The relative importance of these processes is also influenced by crystallinity, with dehydration being favored under completely amorphous conditions (6). At somewhat higher temperatures, fission of the basic structure occurs leading to the formation of the lighter gases. Condensation of the unsaturated compounds leads to the build up of a carbonaceous char. The overall result is the production of scores (7) of compounds whose relative concentrations are strongly controlled by the manner by which the experiments are carried out. Thus it is customary to speak of products in general terms as consisting of a char, tar and volatile gases. These are very indistinct classes. There are small quantities of volatiles in the char. Tar contains substances that are readily volatilizable at higher temperatures. Thus reports of product yields in these terms must be related to the experimental methodology.

Under combustion conditions the initial process involves the ignition of the volatile gases. If oxidation is slow this is followed by the slow combustion of the char. However, in some systems ignition is followed by such rapid temperature increases that practically all the material is volatized and burned and very little residue is left. Under such rapid burning conditions mass transfer effects become controlling and combustion is by layers and the unburnt layers have the same composition as the initial sample.

Lignin is the principal non-polysaccharide found in vegetative matter. It is introduced into municipal solid waste through its presence in wood and yard wastes. It is a polymer with a phenolic structure. There are considerable similarities in structure between lignite and lignin and there may well be similarities in degradation processes. From analytical pyrolysis studies (8)

methoxyphenols, furans as well as low molecular weight volatile gases such as acetone and acetaldehyde have been found. Due to its cross linked aromatic structure char yields are much higher than that for cellulose (9). Plastics are a significant portion of municipal solid waste. Due to its higher heating value (in comparison to MSW) it is of more importance in terms of heating value than its concentration present may suggest . Our thermal analytical studies suggest that most of the plastic present in MSW is polyethylene. The mechanism for the degradation of such compounds is "unzipping" to produce monomer units (such as ethylene from polyethylene). However as in the case with the degradations of all organic solids char formation is a possible side reaction. As for other man-made polymers, they follow the same general pattern, unzipping to smaller fragments and condensation to form char. In common with lignin, cross linked polymers have a greater tendency towards char formation.

We now consider heating values. These are the key parameters for modeling the thermal behavior of energy generating systems. Furthermore, because heats of combustion (on a weight basis) are strongly dependent on elemental composition the complexity of the chemistry which is the characteristic feature of municipal solid waste degradation is considerably simplified. Table II contains a summary of data (10) regarding the heats of combustion of substances commonly found in municipal solid waste. In accordance with their basic cellulosic nature, wood, paper and plants have heats of combustion close to the 4165 cal/g value of α-cellulose (10). The higher value for wood and plants is due to the presence of lignin whose heat of combustion is approximately 6000 cal/gm (10). The lower value for magazine paper can be attributed to the presence of inorganics such as kaolins with very low heating values. Plastics have higher heats of combustion and the lower value for phenol-forma-

Table II: Heats of Combustion of Constituents of Municipal Solid Waste (10)

paper:	newsprint	4433 cal/g
	corrugated box	3915
	magazine	2921
	brown	4034
wood:	birch	4775
	cherry	4370
	fir	5038
	maple	4533
	pine	4592
plants:	grass clippings	4369
	leaves	4439
plastics:	polyethylene	11093
	polypropylene	11082
	phenol-formaldehyde resin	7554
	rubber	10814

ldehyde resins is due to the presence of oxygen. There are a wide variety of methods for the prediction of the heats of combustion (11). A very simple correlation has been found by Shafizadeh and DeGroot (9) and is particularly applicable for the present situation. It has the form

$$\Delta H^{25°}(\text{combustion})\ (\text{cal/gm}) = 94.19(\%\ C) + 55.01$$

As noted by these authors the success of this correlation is due to a fortuitious cancellation of different effects. Measurements at NBS (12) on the variability of MSW samples led to a heating value of 5200 ± 200 cal/g on a dry and ash free basis. This is suggestive of a mixture of cellulose and plastics (polyethylene) with the latter at the 10-15% level.

In the above we have dealt with fairly well defined starting materials. A considerably more difficult problem is the definition of the heat of combustion of the products of pyrolysis and partial oxidation. There is very little literature on this question. In principle if we can enumerate all the compounds that are formed during the pyrolytic process, then since many individual heats of combustion have been measured and others can be estimated with high accuracy, the thermochemistry can be defined. Unfortunately in view of the enormous number of chemicals and the undefined nature of the tar and char it is not possible to proceed in this manner. It is interesting to note that even in an area such as coal pyrolysis this question is still open. In Table III we summarize literature results (9, 13, 14) expressed in terms of percentage char, tar and gases and their heating values. Considering the nature of the experiments and of the starting materials results are not in consistent. The heating value of char is in the 6500-8000 cal/g range or very close to lignite. Char yields are lowest in pure cellulose, higher in MSW and

Table III: Summary of Data on the Heating Values of the Pyrolysis Products from Various Materials

a) Pyrolysis of MSW (Reference 13): Percentage products and heating value (cal/g)

	755 K		922 K		1088.7 K		1200 K	
gases	12%	633	18%	1161	23.7%	1383	24.4%	1320
tars	61%	4670	59.2%	2222	59.7%	2720	58.7%	2440
chars	24.7%	6733	21.8%	6820	17.3%	6411	17.7%	6333

b) Pyrolysis of Wood (Reference 9): Percentage products and heating value (cal/g)

	char		volatiles	
cellulose	14.9%	7052	85.1%	3634
ponderosa pine needles	37%	6588	63%	4294
Douglas fir lignin	59%	7416	41%	4869

c) Pyrolysis of Sawdust (Reference 14): Percentage products and heating value (cal/g)

	813 K		923 K		1033 K		1143 K	
gas	25%	2440	27%	2793	31%	3446	33%	3761
tar	15%	7200	16.5%	7722	18%	7220	17%	7400
char	33%	7676	30%	8027	29%	7900	28%	7800
water	27%		25%		22%		22%	

highest with lignin. The heating value of the gases is much lower than that for tar and char and is due to the presence of CO_2 and CO. There is a large difference between the amount of tar detected in the saw dust and MSW experiments. We are not aware of any chemical basis for this difference. It is suspected that this may arise from differences in carrying out the experiments. The samples of saw dust are probably more closely packed and since the sample size is a factor of 15 larger, total reaction time is much longer.

An important parameter for the present purposes is the heat of pyrolysis. In the case of the sawdust results (14) all of the heating value is recovered. In the MSW experiments (13) considerable organics were lost during the work up of the results, and thus an accurate value is not obtainable. In addition, Kung and Kalekar (15) have fitted a mathematical model to experimental results on wood pyrolysis and derived a heat of reaction of -48.4 cal/g. This is about 1% of the heating value of wood or other cellulosic substances and thus can probably be ignored for the present application. From a more theoretical point of view these results are not unexpected when one compare the heat of combustion of hydrocarbons and their heats of formation. The latter represents the heat of reaction from the elements and for non-oxygenated carbons can be considered the reverse of the pyrolysis reaction.

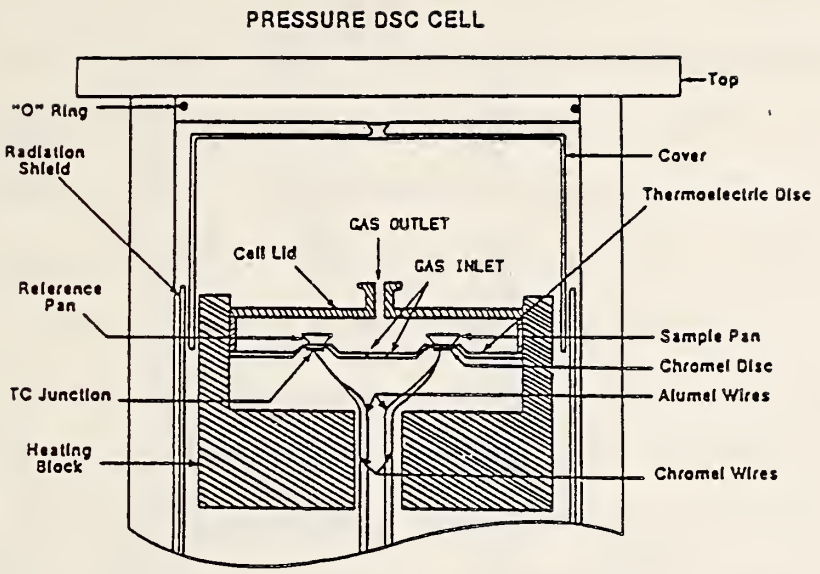
Experimental

In order to increase the information base on the pyrolysis and partial oxidation of municipal solid waste we have carried out a series of experiments using thermo-analytical methodology. At the outset it should be pointed out that for systems such as MSW pyrolysis truly meaningful data can only be obtained from full scale units. The present data and those mentioned earlier can be useful only in the sense of setting limits and suggesting the type of measurements in full scale units that can yield the most significant results.

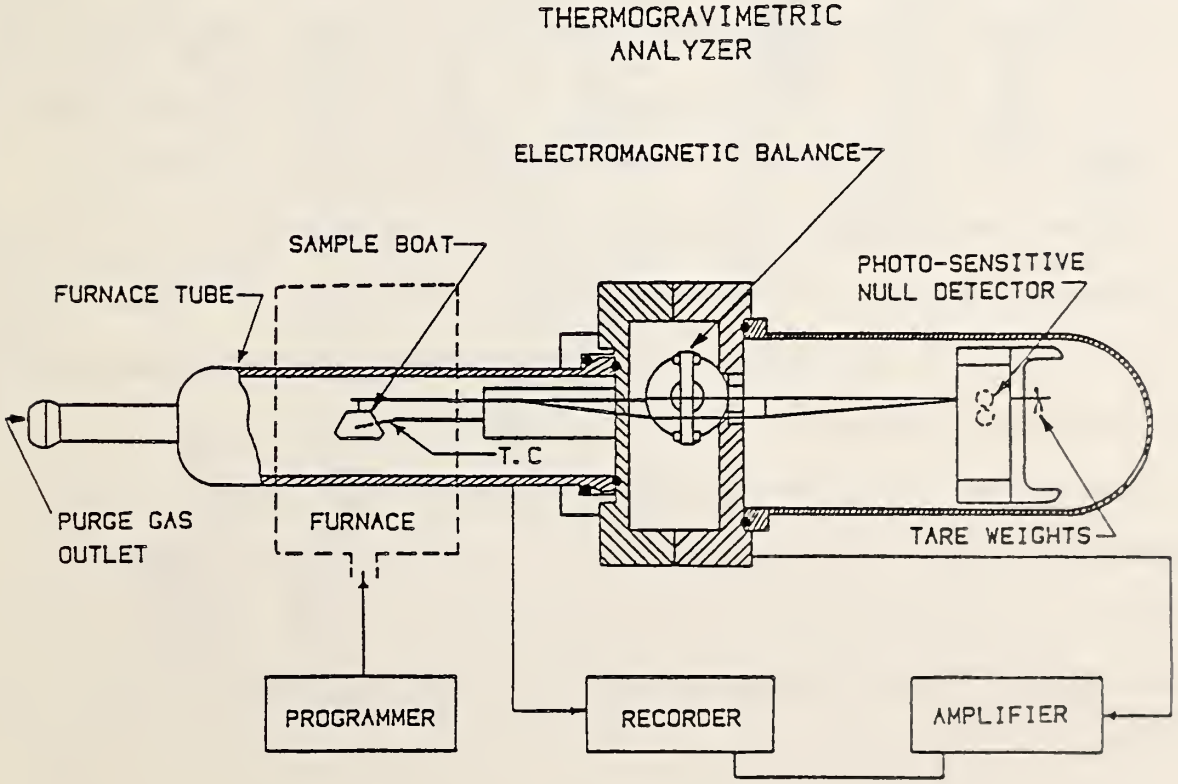
However, as will become clear subsequently, in combination with earlier work our results are very suggestive. In the following we begin by describing the experimental apparatus, this will be followed by a tabulation of the results, and conclude with an interpretation of the observations.

Thermal analytical methods are frequently used today in order to characterize complex condensed phase mixtures (15). The basic technique involves heating a sample at a controlled rate and then observing the response of the system through measurements of an appropriate property (weight change, enthalpy change, dimension, evolved gases, etc). The thermogram so produced is as characteristic as a boiling point or infrared spectrum. Furthermore, through careful analysis one can obtain significant information on the physico-chemical processes that are occurring. A special advantage of the method is that by concentrating on a particular property one drastically simplifies the problem of interpretation. One could for example carry out complete spectroscopic analysis of the sample. In view of the complexity of some systems such data will be extremely difficult to interpret. For the present purposes, our interest will be concentrated on weight loss during pyrolysis and the nature of the gases evolved. The connection between these properties and combustion phenomena is obvious. Indeed, the time scales and conditions are very akin to the situation during the initial steps of the decomposition process in the primary combustion chamber of a starved air incinerator.

The thermogravimetric experiments were carried out with a DuPont 1090 Thermal Analysis System. Some Differential Scanning Calorimetric (DSC) experiments were also carried out with an appropriate attachement. Schematic drawings of the two instruments can be found in Figure II(A-B). In evolved gas analysis, gaseous products are monitored. An apparatus have been con-


PRESSURE DSC CELL
Top
"O" Ring
Radiation Shield
Cover
Thermoelectric Disc
GAS OUTLET
Cell Lid
GAS INLET
Reference Pan
Sample Pan
Chromel Disc
TC Junction
Alumel Wires
Heating Block
Chromel Wires

A


THERMOGRAVIMETRIC ANALYZER
ELECTROMAGNETIC BALANCE
SAMPLE BOAT
FURNACE TUBE
PHOTO-SENSITIVE NULL DETECTOR
T.C
PURGE GAS OUTLET
FURNACE
TARE WEIGHTS
PROGRAMMER
RECORDER
AMPLIFIER

B

Figure II

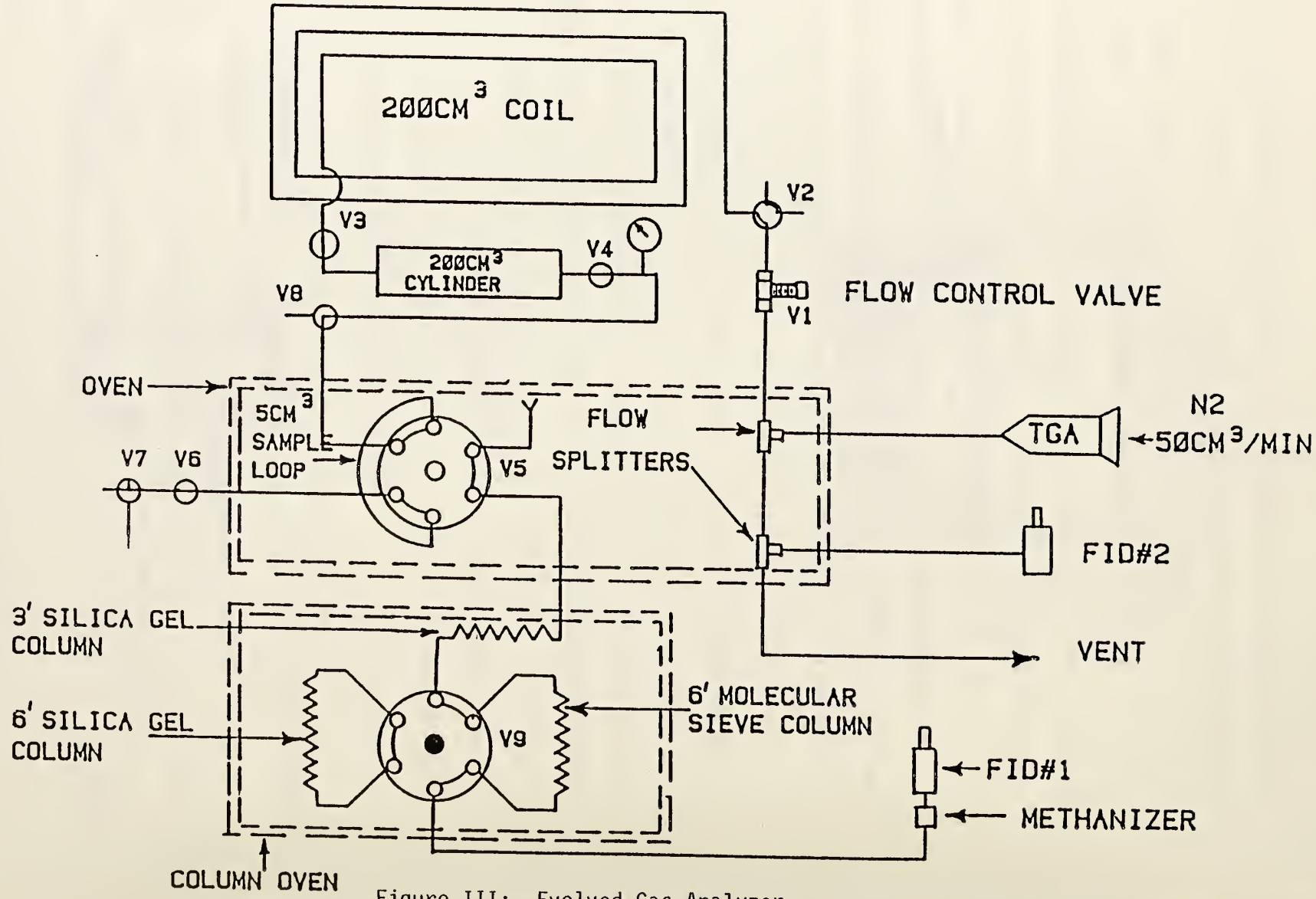
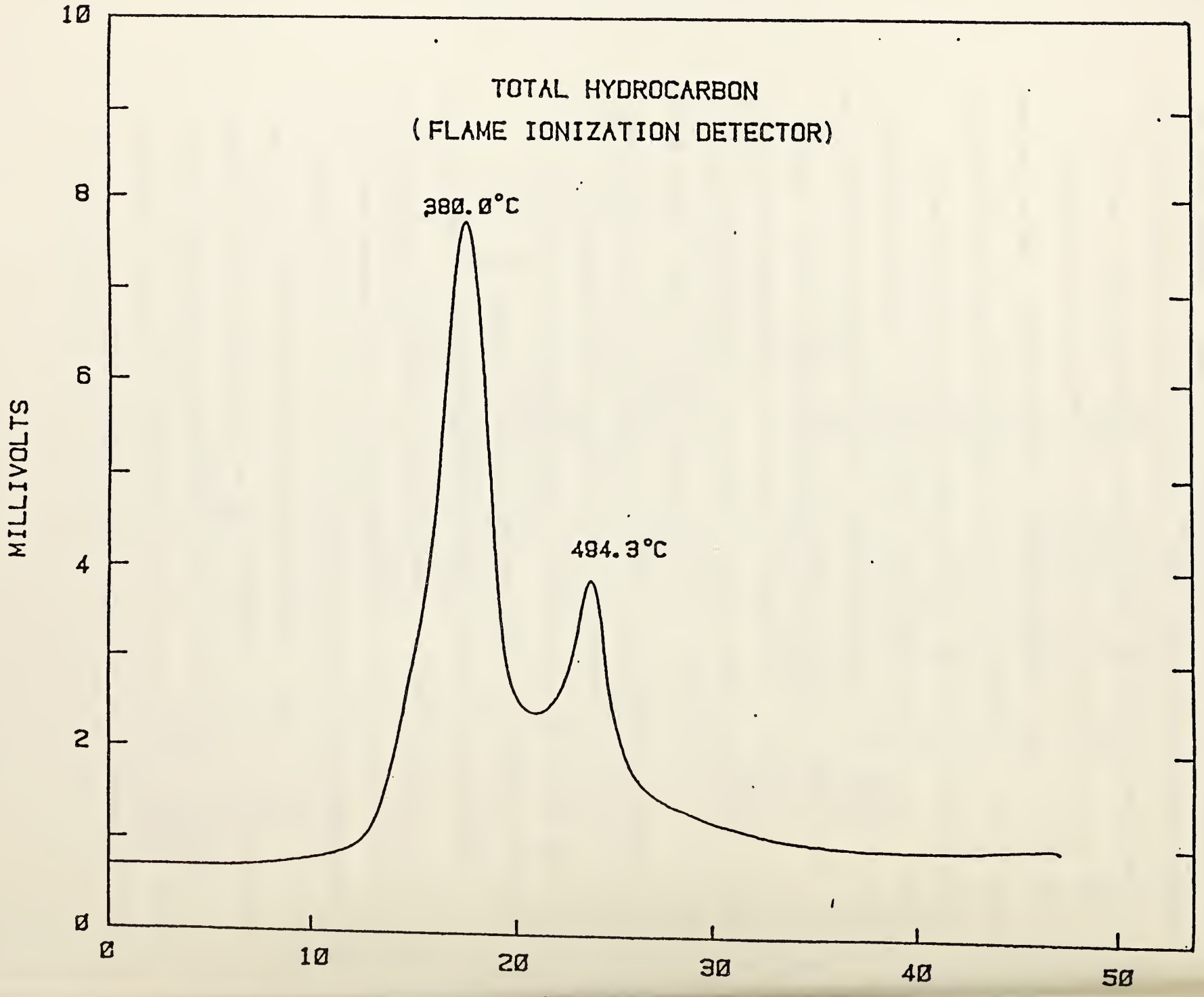


Figure III: Evolved Gas Analyzer

structed and tested. It involved coupling the effluent from the thermogravimatic analyzer with appropriate gas analysis equipment. A schematic of the apparatus can be seen in Figure III. During operation the effluent from the thermogravimetric analyzer, (TGA) is split into three streams. The first stream is fed directly into a flame ionization detector and thus gives a direct measure of the total hydrocarbons that are present. Samples from the second stream are analyzed for the light gases; CH_4, CO and CO_2. The CO and CO_2 are converted to CH_4 by a hydrogenation apparatus with a ruthenium catalyst. This is placed immediately before the flame ionization detector. A third stream was vented so as to control the magnitude of the signal from the FID. We have also attempted to determine H_2 concentration using a thermoconductivity detector. Unfortunately, due to the lower sensitivity of such a detector compared to flame ionization detection we were not able to determine its presence. Nevetheless, there is no question that it is not a major light gas decomposition product. The lines exiting from the TGA were kept at 230 °C. The intention was to make sure that no deposits are formed and all detectable products are analysed. This appears to have been achieved and we believe that there is very little condensation in the lines.

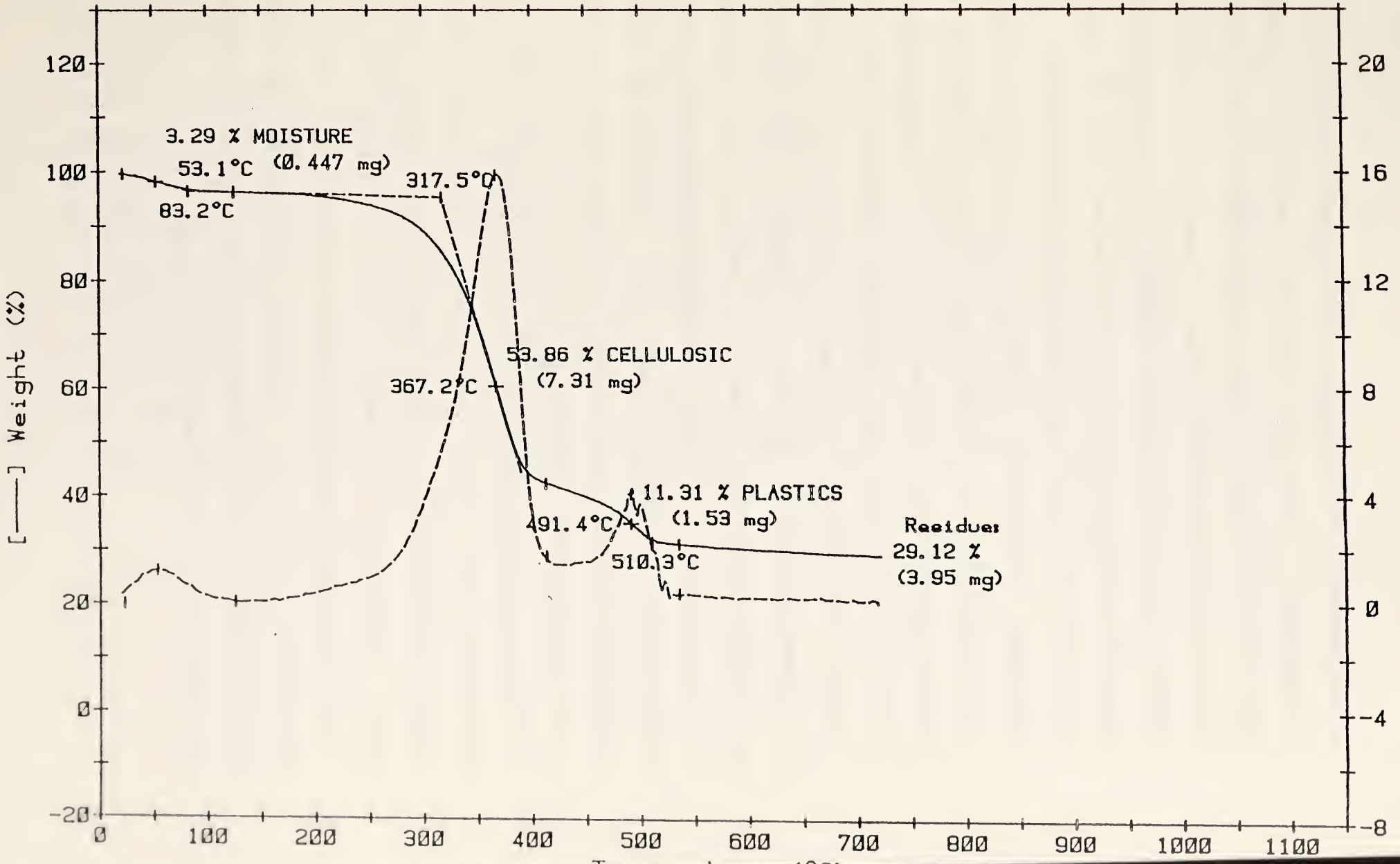
The experimental procedure involves placing a 3-5 milligram sample in the pan of the thermogravimetric analyzer, purging the system for 15 minutes with N_2 to exhaust the air with the atmosphere to be used and then proceeding with the experiments. This involves ramping the temperature at rates of 20 to 100°C/min. The two direct measurements are the thermogravimetric and flame ionization results. The former data represent the weight lose as a function of temperature (or a function of time). Characteristic traces can be seen in Figures IV and V. Note the presence of two distinct processes. The first is due to the decomposition of the cellulosic component while the second is due

Figure IV Total Hydrocarbon (Flame Ionization Detector)



Sample: RDF D1B2A2

Figure V: TGA



to the degradation of the plastic. This has been established through the use of neat samples. In the case of the evolved gas analysis, the direct FID results show the analogous two peaks which resemble the derivative curves. These are due to the gases first from the decomposition of the cellulosic components and then that from the plastic(s). Note the much larger relative amount of the latter in comparison to the thermal analytical trace. This is due to the higher sensitivity of the flame ionization detector to pure hydrocarbons. The stream (see Figure III) that was used to determine quantitative amounts of CH_4, CO, and CO_2 contain information regarding the time history of the evolution these gases. Since this information was not desired we mix the gas in a small 200 cc cylindrical chamber which was initially evacuated. The volume of the chamber was close to that of the lines. Both are commensurate with the flow rate. For example, if flow rate in this stream was 5 cm^3/min, then with a volume of 200 cm^3 experiments were carried out for 40 minutes. When all the gases in the lines are dumped into the chamber complete mixing was achieved. A small sample ~ 5 cm^3 was then taken for analyses and replicate runs were used for checking results. All residue left in the thermogravimetric analyzer was either oxidized in place or in a differential scanning calorimeter. The latter leads to a heating value of the char and was of the order of 7000-8000 cal/g, a characteristic value. The remnant was then weighed. In either case the amount of char is thus determined. A summary of all our results can be found in Table IV-VI. These include experiments with heating rates of 20-100 C/min and involve studies with newsprint, filter paper, plastic, and sawdust as well as the RDF samples mentioned earlier. Most of the experiments were carried out with the latter. The reason for this will become obvious subsequently.

Table IV: Pyrolysis of "Pure" Substances

Property	Samples: Filter Paper 20°/min	Filter Paper 20°/min	Sawdust 20°/min	Sawdust 100°/min	Polyethylene 20°/min	Newsprint 20°/min	Newsprint 20°/min
Total wt (mg)	4.11	4.35	3.72	3.77	4.69	3.96	3.69
non combustibles	≤ 1%	≤ 1%	.29	.65	.02	≤ 1%	≤ 1%
char (mg-C)	.39	.49	.50	.52		.512	.484
% carbon-combustibles	9.5%	11.3%	14.6%	13.9%		12.9%	13.1
FID Sensitive Org(mg-C)	.55%	.48%	.38%	.51%	3.75	.64	.62
% carbon-combustibles	13.5%	11.1%	11.1%	13.8%	80%	16.2	16.9
CO (mg-C)	.20	.23	.23	.25		.20	.18
% carbon-combustibles	4.8%	5.3%	6.7%	6.1%		5.1%	5.0%
CO_2 (mg-C)	.12	.14	.08	.08		.07	.07
% carbon-combustibles	2.9%	3.2%	2.43%	2.2%		1.8	1.9
CH_4 (mg-C)		.04					
% carbon-combustibles		9%					
Total carbon (mg)	1.26	1.32	1.19	1.36	3.75	1.42	1.35
% carbon-combustibles	30.8%	30%	34.6%	36.5%	80%	35.8%	35.6%

Table V: Summary of Data on Municipal Solid Waste Pyrolysis

RDF Sample number							
Property	1	1	1	2	2	2	3
Scan Rate	20°/min	20°/min	100°/min	20°/min	20°/min	100°/min	20°/min
total wt (mg)	3.68	3.83	5.27	4.24	3.87	4.44	4.01
non combustibles	.56	.37	2.21	.66	1.17	.73	.85
char (mg, carbon)	.33	.72	.46	.34	.34	.48	.59
% carbon-combustibles	11%	20%	15%	9.5%	11.3%	12.9%	18.7%
FID Sens. Org. (mg, carbon)	.67	.75	.62	.66	.62	.80	.48
% carbon-combustibles	21.4%	21.6%	20.2%	18.9%	20.1%	21.5%	15.2%
CO (mg, carbon)	.15	.16	.20	.13	.14	.15	.12
% carbon-combustibles	4.8%	4.6%	6%	3.6%	4.5%	4%	3.7%
CO_2 (mg, carbon)		.08	.20	.10	.13	.16	.20
% carbon-combustibles		2.3%	6%	2.8%	4.2%	4.1%	6.3%
CH_4 (mg, carbon)	.04		.02	.06		.023	
% carbon-combustibles	1.3%		.6%	1.7%		.6%	
Total carbon (mg)	> 1.15	1.71		1.24	1.23		1.39
% carbon, combustible	> 36.8%	49.4%	48%	34.6%	39.9%	42.8%	43.9%

3	4	4	5	5	6	7	7
100°/min	20°/min	100°/min	20°/min	20°/min	20°/min	20°/min	20°/min
4.32	3.37	4.21	3.50	3.86	3.63	4.64	3.66
1.14	.62	.74	.41	.43	1.06	1.16	1.72
.43	.34	.41	.39	.45	.25		.16
13.5%	11%	11.8%	12.6%	13.1%	9.7%		9%
.98	1.07	.48	.50	.57	.58	.84	.60
30.8	35%	13.8	16.3%	16.66%	22.6%	24.1%	31%
.28	.13	.10	.17	.20	.13	.13	.11
8.3%	4.3%	2.8%	5.5%	5.8%	5.0%	3.7%	5.6%
.27	.11	.10	.09	.15	.08	.12	.07
8.1%	3.2%	2.8%	2.9%	4.4%	3.1%	3.4%	3.6%
.046		.02					
1.4%							
1.96	1.55	1.09	1.15	1.37	1.04		.94
61.6%	54%	31.4%	37.3%	39.9%	40.4%		48%

8	8	9	9	10	10	Average
20°/min	20°/min	20°/min	20°/min	20°/min	20°/min	
4.52	3.69	3.85	3.60	4.05	3.91	
.95	.35	.71	.89	.40	.46	
.52	.33	.46	.29	.40	.35	
14.5%	10%	14.6%	10%	11%	11%	12.5%
.63	.42	.67	.68	.86	.67	
17.7%	14%	21.4%	22.8%	23.6%	20%	21.4%
.14	.13	.09	.13	.13	.14	
3.9%	4.3%	3.0%	4.3%	3.6%	4.0%	4.6%
.12	.09	.07	.06	.10	.08	
3.5%	3%	2.2%	2%	3.0%	2.2%	3.7%
.03		.08		.05		
1.1%		2.6%		1.3%		
1.41	.97	1.29	1.56	1.43	1.24	
39.4%	32.3%	41.2%	39.1%	40.8%	35.9%	42.2%

Table VI: Summary of Data on the Oxidation of RDF and Constituents

Material	Conditions	CO_2	CO	FID Organics
sawdust	20°/min; air	47%	0	.5%
	20°/min; 10% O_2 in N_2	44%	0	.6%
newsprint	100°/min; air	34%	4.5%	4%
	100°/min; air	40%	3.5%	6%
filter paper	20°/min; air	45.4%	1.5%	
	20°/min; 10% O_2	40.4%	1%	2%
	100°/min; 10% O_2	35.1%	2%	3%
polyethylene	20°/min; air	43%	8%	
RDF	20°/min 10% O_2	49.9%	.6%	
	20°/min 10% O_2	51.2%	.6%	
	20°/min 10% O_2	51.3%	.6%	
	20°/min 5% O_2	43.8%	3.2%	
	20°/min 2% O_2	29%	4.4%	

These experiments involve a multiplicity of measurements and turned out to be difficult to carry out. The main problem was due to the thermgravimetric analyzer being constructed in such a manner that it could not maintain a pressure very much above ambient. Without a large pressure drop, the flow rates through our three lines, vent, FID and light gas analysis, had a tendency to vary. This is probably the main source of experimental scatter in these experiments. We have attempted to minimize this effect by constantly monitoring the flow rate and calibrating immediately before and after the experiments with a standard mixture.

The results in Table IV involve a number of the elements in municipal solid waste. For the present purposes there can be considered to be the "pure" components, whose properties do not vary greatly. Thus the results serve as a measure of the accuracy and precision of our determination. On this basis we expect scatter about mean values of about 15%. For all these substances the amount of non-combustibles is close to minimal. Polyethylene is different than all the other organics in leaving no char and with a high carbon content of 80%. The calculated value is 85.7%. Here again, we have a marker of the accuracy of our determinations. The other organics are all essentially cellulosic in nature and as could be expected have considerable similarities. In all cases we do not collect all of the carbon that is available. Cellulose with an empirical formula of $C_6H_{10}O_5$ has 44% carbon. Newsprint has been found to contain 49% carbon (10). Sawdust is probably in an intermediate position. The consequence is that we are missing about 14% of the available carbon in all three cases. Most if not all this missing carbon must be volatile material tied to oxygen groups. Most such compounds are not detectable with the flame ionization detector. Specifically the groups of interest are acidic, aldehydic and alcoholic moieties. Actually the FID

detector is not completely insensitive to the latter. The sensitivity factor for methanol being about 0.3 to that for methane. An important question is the distribution of these compounds. An examination of the structure of cellulose show three alcohol and one polyether linkage (O-C-O). Note that in the absence of oxygen the only possibility of acid formation is from the polyether linkage. The original C-O linkage can then appear in our system as either alcohols or aldehydes and ketones. The ratio of alcohol and carbonyl groupings compared to the acid is 3 to 1. It is interesting to note that our CO and CO_2 ratio in our filter paper study is of the order of 2 to 1. This is in line with the greater lability of organic acids. On this basis a zeroth order approximation for our undetected carbon is a 3 to 1 mixture of CH_2O (formaldehyde) and CH_2O_2 (formic acid). Actually in terms of heating values we could have expressed these as H_2 + CO and H_2 + CO_2 respectively since the heat of reaction for these processes is negligible. Thus we postulate the carbon oxygenated products from our filter paper pyrolysis to consist of on a carbon weight basis of 10.2% equivalent formaldehyde and 3.4% formic acid. Note that no claim is made that such compounds are actually present in these proportions. Rather, it is the characteristic groups that are of interest. On a similar fashion we can consider our FID results as indicative of the concentration of C_2H_4 or equivalently CH_2 group present. The resulting mixture from cellulose decomposition is thus summarized on Table VII. In deriving these numbers we have also invoked mass balance for oxygen. Obviously in pyrolytic situations oxygen must be bound. Since we have accounted for all the carbon oxygen structures all that is left is water. Interestingly, this leads to a satisfactory mass balance of H_2 and supports our suggestion that under the present conditions hydrogen is not a major product. We can now use this composition to calculate the heat of combustion of the reaction products. The

numbers are given in the second column of Table VII. The approximate nature of such computations must be emphasized. We have for example lumped the alcohols in with our FID hydrocarbons and formaldehyde. However it is possible to demonstrate that no large errors are introduced since the lowered sensitivity in the FID is matched by the lower heats of combustion of C-OH groups. Futhermore, we do arrive at a number that is fairly close to the heat of combustion of cellulose. Thus one suspects that the heat of pyrolysis is very close to zero.

We now consider municipal solid waste samples. Most of our work was carried out with these mixtures. This was due to the fact that the mixtures are quite heterogeneous and problems with respect to reproducibility are expected to be important. This is indeed the case and can be established through inspection of the data from Table V. It is clear that the scatter of the results is far in excess of the results from our "pure" samples. We suspect that this is due to the small samples used in these experiments having an amplifying effect on the heterogeneity of the mixture. With the larger samples used in the earlier NBS calorimetric experiments it is probably much easier to obtain a representative sample. In the present case, homogeneity for each individual run is difficult to achieve. This is readily demonstrated from our thermogravimetric and evolved gas analysis curves where the two peaks which we have earlier identified as that due to the decomposition of cellulosics and polyethylene respectively showed considerable variance. There is apparently some degree of correlation between large measured total carbon concentrations and high levels of plastics. This is however not the complete story since it is not easy to make an exact distinction.

Table VII: Approximate Composition and Heats of Combustion of Products from Cellulose Pyrolysis

Products	Wt%		Heat of Combustion cal/g
CH_2 group (as C_2H_4)	14.3	(11293)	1614
C=O group (as (H_2CO)	24.8	(4138)	1026
O-C=O group (as H_2CO_2)	12.8	(1333)	171
CO_2	11.1		
CO	11.7	(2416)	283
C	11.4	(7837)	893
H_2O	13.5		
			3987
missing H_2 ~ .4%		(28900)	115
			4102

In any case, we believe that an average of all the results will lead to representative values which are appropriate to the pyrolysis products from heated municipal solid wastes. The results are included in the next to last column of our data on Table V. It is interesting to note that our average carbon content, 42.2%, is 12.8% less than the value of 55% given as the approximate carbon content of the combustible portion of the municipal solid waste used in these studies in the earlier NBS report. This is almost the same number that we obtained from the difference between calculated and detected carbon in cellulose decomposition. Furthermore, we note that the percentage of carbon as char from cellulose and municipal solid waste pyrolysis are very close. Finally, the carbon from the FID sensitive organics is about 11% higher than the value from the filter paper studies. When all of this information is coupled with our earlier observation that polyethylene decomposition leave no char, we believe that these results demonstrate that in the pyrolysis of municipal solid waste the chemical process is simply the depolymerization of the constituent fractions with out large synergestic effects. The presence of large quantities of inorganic impurities does not appear to have a major influence on the nature of the decomposition process. Of course all this is based on rather gross observations. It is entirely possible that if one looks at the individual compounds or groupings significant differences may occur. At the present level however these considerations are unimportant. Table VIII contains a summary of the constituents and the heats of combustion of the various components in the pyrolysis products from MSW combustion. Here we have simply distributed the three undetected oxygenated substances in the same manner as in cellulose decomposition. The rationale behind the assignments has been given earlier in the discussion on the heats of combustion of the products from cellulose pyrolysis. On this basis,

Table VIII: Approximate Composition and Heats of Combustion of Products from Municipal Solid Waste Pryolysis

Products	Wt%		Heat of Combustion cal/g
CH_2 group (as C_2H_4)	25	(11293)	2823
C=O group (as H_2CO)	18.5	(4138)	766
O-C=O group (as HCOOH)	9.5	(1333)	127
CO_2	13.6		
CO	10.8	(2416)	260
C	12.5	(7837)	980
H_2O	10.0		
			4956

we get a total heating value of 4956 cal/g or very close to the heating value of the original MSW of ~ 5200 cal/g. The pyrolysis reaction is very close to thermally neutral.

Table VI contains data on the oxidation of MSW and its constituent parts. The key observation is the ease of ignition of MSW samples. One notes that even with concentrations of oxygen as low as 2%, half of the municipal solid waste is converted to carbon dioxide. This is also indicative of the "all or nothing" nature of the oxidation process. That is, one does not proceed smoothly from reactant to ever more oxygenated products. Instead, ignition occurs and the very high temperature converts practically all the available carbon compounds into carbon dioxide. Of some interest is the high yield of hydrocarbons in polyethylene oxidation. The hydrocarbon effluents from polyethylene pyrolysis are apparently more difficult to ignite. In a complex mixture such as municipal solid waste, however the high temperature attendant upon the ignition of cellulose will in most cases ignite the polyethylene. Thus the observations on polyethylene oxidation must be interpreted with care.

Discussion

We now consider our experimental results within the context of earlier work. This is particularly significant because of the widely diverging experimental configurations. In our experiments sample sizes are extremely small; of the order of 3-5 milligrams. As soon as the material is volatilized it is diluted and the conditions are such that possibilities of subsequent reactions are minimized. This is very similar to the experimental configuration of Shafizadeh and DeGroot (9) and their char yields of 14.9% is reasonably close to our value of 10.5%. On the other hand the results of Hoffman and Fitz deal with pyrolysis in a retort and with a sample of 168 grams. This is equivalent to a scale up of a factor of 40000. Nevertheless one notes on a

weight basis the char yields of 17% to 25% and more important, tar yields in the 60% level. This is in very close accord with our observations. In both cases the intermediate tar has not had time to decompose to light gases or condense to form char. It is likely that there are compositional differences among the three broad categories. Indeed the observed H_2 concentration in the retort experiment is probably correlatable with the somewhat larger char yields. For the present purposes the lack of gross differences despite profound changes in experimental configuration is encouraging. It should be noted that in the retort experiment, the reported temperature is at best the temperature of the wall of the reaction. Unfortunately, no time information is given. Thus detailed comparison becomes impossible. Note that the higher temperature runs are undoubtedly also effected by the much shorter residence time of the volatilate. This may partly account for the lower char yields at the higher temperature.

A different situation is encountered in the sawdust experiments. Here samples of 2500 gms are used and yields of char and light gases are considerably higher than from the experiments with municipal solid waste. It is possible that the very small size of the sawdust increases the possibility of initial volatilates reacting and thus producing less tar.

We now consider the situation in the primary combustion chamber of a starved air incinerator. The physical process involves the contact of low temperature under fired air with a mixture of char and refuse. There is no question that the refuse will ignite. The high temperature will assist the combustion of the char, although we suspect that some char will be unburnt. Thus at a certain level above the grate all oxygen will be exhausted and we will have a rising current of hot N_2, CO_2 and H_2O which will pyrolyze the layers of refuse. The initial composition will be that which we have deter-

mined in the course of our thermal analytical experiments. As the pyrolysis gases rise through the refuse they will face temperature at or below the 350°C level where pyrolysis begins. The important question is whether further cracking occurs. The results of Hoffman and Fitz may set an upper limit. Note that although sample size in an actual incinerator is probably a factor of 1000 more, the linear length is changed by a factor of 10. Since in an incinerator the heat source is within the system itself and with the N_2 in the air as a diluent, the actual time for pyrolysis of the volatilates (order of seconds), in a starved air incinerator is probably not much longer than in the retort. Furthermore there is the effect of the diluent N_2 in reducing the possibility of condensation processes. Thus we would take our values for the quantity of char as a lower limit while the data of Hoffman and Fitz will be close to the upper limit.

As the pyrolyses products escape from the bed the presence of over fired air will cause further combustion. The overall effect will be to heat the gas and lower the heating value. Physically, we envision a diffusion flame mechanism. A given portion of the pyrolysis gas will be oxidized while the remainder will be raised to a higher temperature. As before an important question is whether there will be extensive cracking. At this time, no definitive conclusions cannot be drawn. At the quoted temperatures we suspect extensive cracking of oxygenated compounds will occur. Fortunately the degree of cracking of the pyrolysis gases does not have much an effect on the heating values. For example the cracking of acetaldehyde follows the reaction stochiometry $2CH_3CHO \rightarrow 2CO + C_2H_4 + 2H_2$ and is a thermally neutral process. Indeed, the manner by which we have expressed the results of our pyrolysis experiments suggest this approximation. That is, we can express our equivalent HCHO and HCOOH as cracked to H_2, CO and CO_2. On the other hand the

equivalent C_2H_4 will be carried into the secondary combustion chamber. It is of course possible to define the composition in terms of an equilibrium hypothesis. However residence times of 1 sec at 800-900°C is insufficient to crack olefins or aromatics. Indeed, it is at this temperature that one begin to make the lighter olefins from larger hydrocarbons in naptha crackers.

Summary and Recommendation

Experiments have been carried out with the aim of defining the products of incomplete combustion of municipal solid waste. In combination with earlier work we find the pyrolysis process to be close to thermally neutral. The minimum char content is of the order of 10% (wt. basis) of the total available combustible organics. The volatilates can be expressed in terms of equivalent quantities of C_2H_4 (28.6%), HCHO (21.1%), HCOOH (10.9%), CO_2 (15.6%) and CO (12.3%). For higher char yields reduce equivalent quantities of C_2H_4. The equivalent HCHO and HCOOH will under sufficiently severe condition be cracked to CO, CO_2 and H_2. Oxidation will lead to complete conversion of stochiometric quantities of fuel to CO_2 and H_2O. It should be emphasized that the above represent a gross simplification to a very complex chemical situation. In conjunction with an appropriate model it can best serve as a guide for the kind of monitoring that is most appropriate for the optimization of such devices.

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Thermal analytical measurements on the pyrolytic and oxidative decomposition of municipal solid waste and its constituent parts (cellulose, sawdust, newsprint and polyethylene) have been carried out. Under pyrolytic conditions thermogravimetric analysis of municipal solid waste indicate minimum yields of char in the 10% range. Evolved gas analysis yielded information regarding the nature of the volatilate in terms of total FID sensitive hydrocarbons, CO, CO_2 and CH_4. From material balance considerations it is concluded that the volatilate include large quantities of acidic carbonyl and alcohol compounds. The total quantity of volatilates not including the directly analyzed light gases is of the order of 60%. The overall process is thermally neutral. This is in good agreement with measurements using larger samples. Under oxidative conditions MSW ignited very easily and reaction goes rapidly to completion. Combination of the experimental data and literature information leads to a description of the chemical processes in starved air incineration.

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Evolved gas analysis; refuse derived fuel; pyrolysis; combustion; oxidation; incineration; cellulose; depolymerization

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